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IRON(II) FLUORIDE

[7789-28-8]

Formula: FeF_2 ; MW 93.842; also, a tetrahydrate $\text{FeF}_2 \cdot 4\text{H}_2\text{O}$ (MW165.90) [13940-89-1] is known.

Synonym: ferrous fluoride

Uses

Iron(II) fluoride is used as a catalyst in organic fluorination reactions. Other applications are in ceramics; and in the preparation of fluoride salts of other metals.

Physical Properties

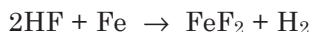
White tetragonal crystal; density 4.09g/cm^3 ; melts at 1100°C ; slightly soluble in water; insoluble in ethanol and ether; dissolves in dilute hydrofluoric acid. Tetrahydrate crystals are hexagonal shape; density 2.20g/cm^3 ; decomposes at 100°C .

Thermochemical Properties

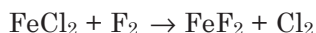
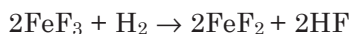
ΔH_f°	-170.0 kcal/mol
ΔG_f°	-159.8 kcal/mol
S°	$20.8\text{ cal/degree mol}$
C_p	$16.3\text{ cal/degree mol}$
ΔH_{fus}	12.43 kcal/mol

Preparation

Anhydrous iron(II) fluoride may be prepared by passing hydrogen fluoride gas over iron at a high temperature:



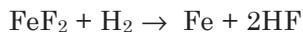
Alternative methods of preparation of anhydrous salt involve the reduction of iron(III) fluoride with hydrogen; or by passing fluorine gas over anhydrous iron(II) chloride in the cold:



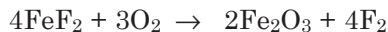
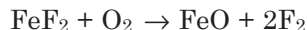
The tetrahydrate may be prepared by dissolving iron metal in aqueous hydrofluoric acid.

Reactions

Iron(II) fluoride is reduced to iron metal when heated with hydrogen or other reducing agents:



When heated with oxygen, it first forms iron(II) oxide which is converted into iron(III) oxide:



Analysis

Elemental composition: Fe 59.51%, F 40.49%. The compound may be analyzed by x-ray techniques. Iron may be analyzed by AA or ICP/AES methods following digestion with dilute hydrofluoric acid and nitric acid and appropriate dilution.

IRON(II) HYDROXIDE

[18624-44-7]

Formula: $\text{Fe}(\text{OH})_2$; MW 89.96

Synonym: ferrous hydroxide

Uses

The compound is used in abrasives; and in pharmaceutical applications.

Physical Properties

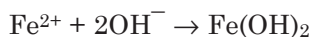
Pale green hexagonal crystals (in partially oxidized form) or white amorphous powder (when pure); density 3.4g/cm^3 ; decomposes on heating; insoluble in water (1.5 mg/L at 20°C), $K_{\text{SP}} 8.0 \times 10^{-16}$; soluble in acids; moderately soluble in ammonium salt solutions; insoluble in alkalies.

Thermochemical Properties

ΔH_f°	-136.0 kcal/mol
ΔG_f°	-116.3 kcal/mol
S°	$21.0\text{ cal/degree mol}$

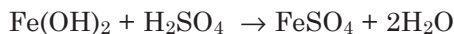
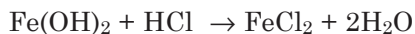
Preparation

Iron(II) hydroxide may be prepared by precipitation of an iron(II) salt solution with caustic soda or caustic potash in the absence of air. Pure compound may be obtained by mixing solutions of caustic potash and iron(II) sulfate—both the solutions made in freshly boiled water—in a reducing atmosphere of hydrogen:



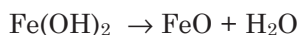
Reactions

Iron(II) hydroxide dissolves in acids forming corresponding salts:



It oxidizes slowly in the atmosphere, eventually forming the reddish-brown hydrated ferric oxide, $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$.

Thermal decomposition in vacuum produces iron(II) oxide:

**Analysis**

Elemental composition: Fe 62.15%, H 2.24%, O 35.61%. The compound may be characterized by x-ray techniques. It may be dissolved in HNO_3 or HCl , the solution diluted appropriately and analyzed for iron by various instrumental techniques (See Iron).

IRON(III) HYDROXIDE

[1309-33-7]

Formula: Fe(OH)_3 ; MW 106.87

Synonyms: ferric hydroxide; hydrated iron(III) oxide.

Uses

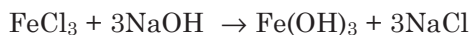
The compound is used in pigments and in water purifications.

Physical Properties

Red-brown amorphous powder; density 3.40g/cm^3 ; soluble in acids; insoluble in water and alcohol.

Preparation

Iron(III) hydroxide is obtained as a brown gelatinous precipitate by adding a strong base to a solution of iron(III) salt:

**Analysis**

Elemental composition: Fe 52.26%, O 44.91%, H 2.83%. The compound may be dissolved in dilute nitric acid and the acid extract analyzed for iron by various instrumental techniques (See Iron).

IRON(III) NITRATE

[10421-48-4]

Formula: $\text{Fe}(\text{NO}_3)_3$; MW 241.87; also exists as nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, MW 404.00 [7782-61-8]

Uses

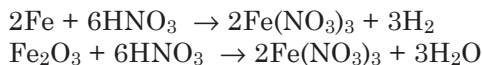
Iron(III) nitrate is used as a mordant for dyeing black and buff. Other applications are in tanning; weighting silks; and in preparation of analytical standards.

Physical Properties

The nonahydrate form occurs as grayish-violet crystal; density 1.68 g/cm^3 ; hygroscopic; decomposes at 47°C ; very soluble in water, alcohol and acetone.

Preparation

Iron(III) nitrate is prepared by the action of nitric acid on iron filings or iron oxide followed by crystallization:



Analysis

Elemental composition: Fe 23.09%; N 17.37%, O 59.54%. The aqueous solution analyzed for iron by various instrumental methods (See Iron) and for nitrate by nitrate-ion selective electrode or ion chromatography following appropriate dilution.

IRON(II) OXIDE

[1345-25-1]

Formula: FeO ; MW 71.844

Synonyms: ferrous oxide

Occurrence and Uses

Iron(II) oxide occurs in the mineral, wustite. It is used in the manufacture of heat-absorbing green glasses. It also is used in ceramic mixtures and enamels; and as a catalyst.

Physical Properties

Black cubic crystal; density 5.7 g/cm^3 ; melts at $1,377^\circ\text{C}$; insoluble in water and alkalis; dissolves in acids.

Thermochemical Properties

ΔH_f°	-65.04 kcal/mol
ΔH_{fus}	5.74 kcal/mol

Preparation

Iron(II) oxide may be prepared by thermal decomposition of iron(II) oxalate:



The product obtained above is impure, that may contain small quantities of triiron tetroxide, Fe_3O_4 and carbon.

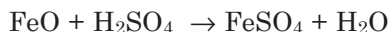
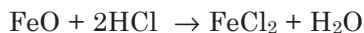
The oxide is stable above 575°C . Thus, it can be prepared by heating iron with oxygen under appropriate pressure at 575°C . Also, iron(II) oxide has been prepared by saturating the fused triiron tetroxide with iron, powdering the mixture, followed by magnetic separation of the oxide from excess iron (Sidgwick, N.V. 1950. *The Chemical Elements and Their Compounds*, Vol.2, pp 1328, Oxford: Clarendon Press).

Reactions

Iron(II) oxide readily oxidizes to iron(III) oxide. The oxide is stable at high temperatures. Upon cooling, it decomposes to triiron tetroxide and iron:



The oxide is basic in nature. It dissolves in acids forming the corresponding iron(II) salts of acids:

**Analysis**

Elemental composition: Fe 77.73%, O 22.27%. The oxide may be characterized by x-ray methods. The metal may be determined by dissolving the compound in dilute nitric acid, diluting the extract appropriately and analyzing by AA or ICP/AES techniques.

IRON(III) OXIDE

[1309-37-1]

Formula: Fe_2O_3 ; MW 159.70

Synonyms: ferric oxide, hematite, red iron oxide, ferric sesquioxide

Occurrence and Uses

Iron(III) oxide occurs in nature as the mineral hematite. It is the principal

ore of iron from which the metal and its alloys are produced. Also, this oxide occurs in the mineral, limonite, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. An important application of this compound involves producing red, orange, and yellow pigments. Other applications are in coatings for metals, steel and rubber; in ceramics; and as a catalyst for oxidation reactions.

Physical Properties

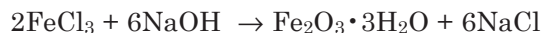
Reddish-brown hexagonal crystal; refractive index 2.91; density 5.25g/cm^3 ; Moh's hardness 6.0; melts at 1565°C ; insoluble in water; dissolves in acids.

Thermochemical Properties

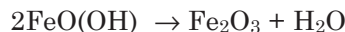
ΔH_f°	-197.0 kcal/mol
ΔG_f°	-177.8 kcal/mol
S°	20.9 cal/degree mol
C_p	24.8 cal/degree mol

Preparation

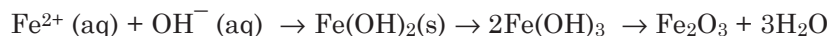
Iron(III) oxide is prepared as a reddish-brown hydrated precipitate by treating an aqueous solution of an iron(III) salt with caustic soda:



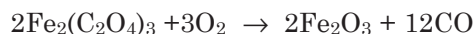
It also is obtained by thermal decomposition of iron(II) sulfate or the brown oxide hydroxide:



The oxide is prepared in industrial scale by first precipitating iron(II) hydroxide $\text{Fe}(\text{OH})_2$ by treating aqueous solutions of iron(II) sulfate and caustic soda. The $\text{Fe}(\text{OH})_2$ is then oxidized to iron(III) hydroxide by aeration. The latter is dehydrated by heating:

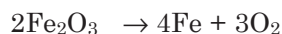


It also is produced by ignition of iron(III) oxalate and iron carbonyls:



Reactions

Iron(III) oxide decomposes to its elements when heated at elevated temperatures:

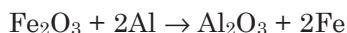


The oxide is reduced by most reducing agents. Reaction with carbon monox-

ide at elevated temperatures (that occurs in the blast furnace) gives metallic iron. The overall reaction is mildly exothermic ($\Delta H_{\text{rxn}} -113.4$ kcal/mol):



It also is reduced by powdered aluminum at elevated temperatures, forming aluminum oxide and metallic iron:



The reaction is highly exothermic and becomes self-sustaining after ignition. When heated with sand in an electric furnace, iron(III) oxide forms ferrosilicon alloy. When heated in a vacuum at 1,000°C, it forms triiron tetroxide, Fe_3O_4 .

Analysis

Elemental composition: Fe 69.94%, O 36.06%. The oxide may be characterized by physical and magnetic properties and by x-ray methods. Iron may be analyzed by various instrumental techniques following acid digestion and appropriate dilution (See Iron).

TRIIRON TETROXIDE

[1317-61-9]

Formula: Fe_3O_4 ; MW 231.53; exhibits a tendency to form nonstoichiometric structure.

Synonyms: iron(II,III) oxide; ferrosoferric oxide; magnetite; lodestone

Occurrence and Uses

Triiron tetroxide occurs in nature as the mineral magnetite, the magnetic oxide of iron. This mineral along with hematite is used as the starting material for producing iron, steel and other ferro-alloys.

Physical Properties

Black cubic crystal or amorphous powder; refractive index 2.42; density 5.17 g/cm³; Moh's hardness 6.0; melts at 1,597°C; insoluble in water, soluble in acids.

Thermochemical Properties

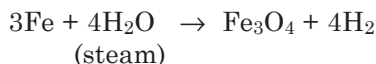
ΔH_f°	-267.3 kcal/mol
ΔG_f°	-242.7 kcal/mol
S°	35.0 cal/degree mol
C_p	34.3 cal/degree mol
ΔH_{fus}	33.0 kcal/mol

Preparation

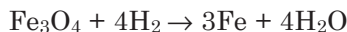
Triiron tetroxide is obtained from its natural mineral magnetite. In the laboratory the compound may be prepared by adding sodium hydroxide solution to an aqueous solution of 1:2 molar mixture of ferrous and ferric salt. (i.e., 1 mol FeCl_2 + 2 mol FeCl_3). The resulting black precipitate of the hydroxide on heating dehydrates to give triiron tetroxide:



Also, the tetroxide may be produced by partial oxidation of iron or iron(II) sulfate by heating under limited amount of air. Another method of production involves heating iron metal with steam:

**Reactions**

Triiron tetroxide, when heated at elevated temperatures with a reducing agent such as hydrogen or carbon monoxide in the absence of air, produces metallic iron:



Partial reduction gives iron(II) oxide. When treated with concentrated acids, the tetroxide dissolves in acids forming mixtures of iron(II) and iron(III) salts:

**Analysis**

The mineral magnetite may be characterized from its physical and magnetic properties and by x-ray methods. The iron content in the oxide may be determined by AA, ICP/AES, x-ray fluorescence and other instrumental techniques (See Iron).

IRON(II) SULFATE

[7720-78-7]

Formula: FeSO_4 ; MW 151.91

Synonyms: ferrous sulfate; green vitriol

Occurrences and Uses

Iron(II) sulfate is probably the most important salt of iron, as well as the longest-known iron(II) compound. The compound is used as a mordant in dyeing; as a component of writing ink; in electroplating baths; in radiation dosimeters; in lithography and engraving; as a weed-killer; and in water purification. A major application of this compound is in the manufacture of other iron(II) salts including Prussian blue or ferric ferrocyanide. Iron(II) sulfate also is used as a reducing agent and an analytical reagent (in brown ring test for nitrate).

Physical Properties

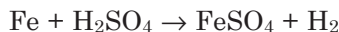
White orthorhombic crystal; hygroscopic; density 3.65 g/cm³; soluble in water (26.6g/100g water at 20°C). The monohydrate is a yellowish-white monoclinic crystal; density 3.0 g/cm³; decomposes at 300°C; soluble in water. Heptahydrate is bluish-green monoclinic crystal; refractive index 1.47; hardness 2 Mohs; density 1.89g/cm³; decomposes at about 60°C; very soluble in water; soluble in absolute methanol; slightly soluble in ethanol.

Thermochemical Properties

ΔH_f°	-221.9 kcal/mol
ΔG_f°	-196.2 kcal/mol
S°	25.7 cal/degree mol
C_p	24.0 cal/degree mol

Production

Iron(II) sulfate in industrial scale is mostly produced in the pickling process as a by-product of the steel industry. It is obtained when the surface of steel is cleaned with dilute sulfuric acid to remove metal impurities. In the laboratory iron(II) sulfate heptahydrate may be prepared by dissolving iron in dilute sulfuric acid in a reducing atmosphere, followed by crystallization:

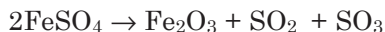


Alcohol may be added to the aqueous solution to speed up crystallization; iron(II) may otherwise oxidize to iron(III) during a slow crystallization process.

Iron(II) oxide or carbonate may be used instead of iron metal to prepare the heptahydrate.

Reactions

The heptahydrate loses three molecules of water on heating at 56°C, forming the tetrahydrate $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$. On further heating the tetrahydrate loses three more water molecules at 65°C, giving monohydrate, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. The latter is stable to 300°C. On further heating anhydrous FeSO_4 is obtained, which on strong heating decomposed to iron(III) oxide and sulfur oxides:



Iron(II) sulfate reacts with concentrated sulfuric acid to form iron(III) sulfate and sulfur dioxide:

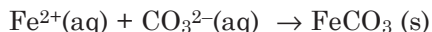


Iron(II) sulfate is a reducing agent. In an aqueous solution, it reduces nitrate and nitrite ions forming a brown ring of $\text{Fe}(\text{NO})\text{SO}_4$. This reaction is applied for qualitative detection of nitrate and nitrite ion in the solution.

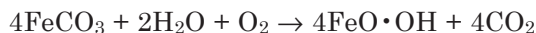
The compound is oxidized by moist air forming basic iron(III) sulfate. Aqueous solutions exposed to air also undergo oxidation; the reaction, however, is very slow. The rate of oxidation increases with temperature and the pH. In alkaline medium, the oxidation is much faster. In solution, it also is oxidized to Fe^{3+} by radiations from radioactive substances. This reaction is utilized to measure the radiation dose in dosimeter solutions.

Iron(II) sulfate forms double salts with the sulfates of ammonium, alkali and alkaline-earth metals (K, Rb, Cs, Mg). Such double salts are obtained by mixing equimolar amounts of these salts followed by crystallization. Some examples are $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's salt), $\text{FeSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{FeSO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$.

When sodium carbonate is added to an aqueous solution of iron(II) sulfate, a white precipitate of iron(II) carbonate is produced. The above reaction is manifested by all iron(II) salts in aqueous solution:



The white precipitate rapidly turns green and then oxidizes to brown $\text{FeO}(\text{OH})$:



Analysis

Elemental composition: Fe 36.77%, S 21.10%, O 42.13%. The water of crystallization in the hydrate salt may be determined by gravimetry. Iron may be analyzed by various instrumental techniques (See Iron).

Sulfate may be analyzed in an aqueous solution of the salt either by ion chromatography or by gravimetry or colorimetry following treatment with barium chloride.

IRON(III) SULFATE

[10028-22-5]

Formula: $\text{Fe}_2(\text{SO}_4)_3$; MW 399.88. Several hydrates are known: monohydrate [43059-01-4]; hexahydrate [13761-89-2]; heptahydrate [35139-28-7]; nonahydrate [13520-56-4]

Synonyms: ferric sulfate; ferric persulfate; ferric sesquisulfate

Uses

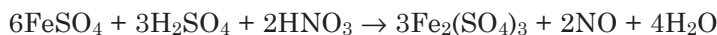
Iron(III) sulfate is used as a pigment; as a mordant in calico printing and dyeing textiles; in sewage treatment; as a coagulant in water purification; in pickling stainless steel; in etching aluminum; and as a catalyst. An important application of this compound is for preparing other iron(III) salts and iron alums. It also is used in pharmaceutical preparations.

Physical Properties

The anhydrous salt constitutes grayish-white rhombic crystals; hygroscopic; density 3.10 g/cm³; slightly soluble in cold water; decomposes in hot water. The nonahydrate is a yellow hexagonal crystalline substance; refractive index 1.54; density 2.10 g/cm³; hardness 2.5 Mohs; decomposes at 400°C; very soluble in water.

Preparation

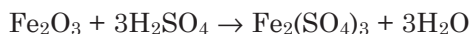
Iron(III) sulfate may be prepared by oxidation of iron(II) sulfate by hydrogen peroxide, nitric acid or any other suitable oxidizing agent. The reaction is carried out in sulfuric acid. Balanced molecular equations for the reactions with hydrogen peroxide and nitric acid are as follows:



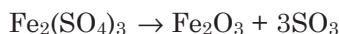
Even in the absence of an oxidizing agent, concentrated sulfuric acid alone can convert iron(II) sulfate to iron(III) sulfate:



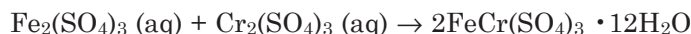
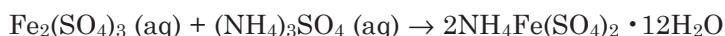
It also may be prepared by treating iron(III) oxide with sulfuric acid:

**Reactions**

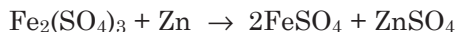
Thermal decomposition of iron(III) sulfate yields iron(III) oxide with evolution of sulfur trioxide:



Iron(III) sulfate readily forms alums with many isomorphous compounds by mixing equimolar amounts of both the salts in aqueous solutions followed by crystallization:



Iron(III) sulfate may be reduced to +2 oxidation state of the metal in solution in the presence of common reducing agents. For example, reaction with zinc in sulfuric acid can produce iron(II) sulfate. The molecular equation is as follows:



Analysis

Elemental composition: Fe 27.93%, S 24.06%, O 48.01%. The water of crystallization in the hydrate salt may be determined by gravimetry. Iron content of the salt may be determined by common instrumental techniques (See Iron). Sulfate can be analyzed in an aqueous solution of the salt by gravimetry or colorimetry after addition of barium chloride solution.

IRON(II) SULFIDE

[1317-37-9]

Formula: FeS; MW 87.911; the pure compound is nonstoichiometric, deficient in iron; the stoichiometric formula may be $\text{Fe}^{2+}_{0.86}\text{S}^{2-}$.

Uses

Iron(II) sulfide occurs in nature as the minerals magnetkies, troillite and pyrrhotine. The most important application of this compound is in Kipp's apparatus as a source for laboratory preparation of hydrogen sulfide. It also is used in paints, pigments, and ceramics and lubricant coatings.

Physical Properties

Colorless hexagonal or tetragonal crystals; density 4.7g/cm³; melts at 1188°C; insoluble in water; soluble in acids (reacts)

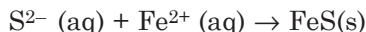
Thermochemical Properties

ΔH_f°	-23.9 kcal/mol
ΔG_f°	-24.0 kcal/mol
S°	14.4 cal/degree mol
C_p	12.1 cal/degree mol
ΔH_{fus}	7.53 kcal/mol

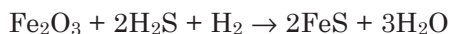
Preparation

Iron(II) sulfide may be synthesized from the elements but the product is contaminated with iron. The reaction is exothermic and the heat of reaction melts iron. Pure sulfide may be obtained by using a slight excess of sulfur: the excess then is distilled off.

The compound also may be precipitated by treating an aqueous solution of an alkali metal sulfide with that of iron(II) chloride or any iron(II) salt solution:

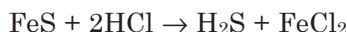


Another method of preparation involves passing a mixture of hydrogen sulfide and hydrogen over iron(III) oxide at about 1,000°C:

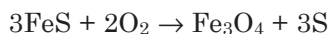


Reactions

Iron(II) sulfide reacts with acids evolving hydrogen sulfide:

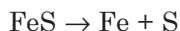


The compound is readily oxidized under moist condition by action of air, forming triiron tetroxide and elemental sulfur:

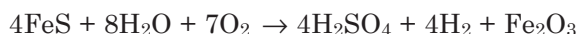


The above reaction is exothermic.

Iron(II) sulfide decomposes to its elements when heated above 1,100°C:



When heated with boiled water, it generates sulfuric acid and hydrogen:



Analysis

Iron(II) sulfide exhibits nonstoichiometric composition. It may be characterized by x-ray. Iron may be analyzed by various instrumental techniques. (See Iron).

IRON(II) THIOCYANATE

[6010-09-9]

Formula: $\text{Fe}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$; MW 226.06; exists as a trihydrate.

Synonyms: ferrous thiocyanate; ferrous sulfocyanate; ferrous sulfocyanide

Uses

Iron(II) thiocyanate is used as an analytical reagent and as an indicator for detecting peroxides in organic solutions.

Physical Properties

Pale-green monoclinic prisms; unstable; readily oxidized on exposure to air; decomposes on heating; very soluble in water; also soluble in alcohol and ether.

Preparation

Iron(II) thiocyanate is obtained as a trihydrate by dissolving iron metal in thiocyanic acid in an inert atmosphere in the absence of air.

Analysis

Elemental composition: Fe 32.47%, S 37.28%, C 13.96%, N 16.29%. The compound may be analyzed by colorimetry following its ready oxidation to red iron(III) thiocyanate. The intense red color produced in acidic pH may be measured by a spectrophotometer or a filter photometer at 460 nm.

KRYPTON

[7439-90-9]

Symbol: Kr; atomic number 36; atomic weight 83.80; a Group 0 (Group 18) element; inert gas element; electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; valence state 0; an uncommon valence state +2 exists for its difluoride; first ionization potential 13.999 volt; six stable natural isotopes are known; most abundant isotope Kr-84. Natural isotopes and their abundances: Kr-78 (0.354%), Kr-80 (2.20%), Kr-82 (11.56%), Kr-83 (11.55%), Kr-84 (56.90%), Kr-86 (17.37%).

Seventeen radioisotopes have been synthesized in nuclear reactions. Among them Kr-85 and Kr-87 have the longest half-lives of 10 and 6 ½ years, respectively, both undergoing beta decay.

History, Occurrence, and Uses

Krypton was discovered by William Ramsay and M.W. Travers in 1898. The element was named krypton, after the Greek word *kryptos* which means hidden. Krypton in trace quantities is found in the earth's atmosphere at a concentration level of about 1.14 ppm. The gas also is found in the spent fuel from nuclear reactors, resulting from fission of uranium and plutonium nuclei. Krypton has been found in Mars' atmosphere in trace concentration.

The commercial applications of krypton are fewer than those of helium or argon. Its principal use is in fluorescent lights. It is mixed with argon as a filling gas to enhance brightness of fluorescent tubes. Other applications are in flash tubes for high-speed photography and incandescent bulbs. Radioactive Kr-85 is used as a tracer to monitor surface reactions. The unit of length, meter was previously defined in terms of the orange-red spectral line of Kr-86.

Physical Properties

Colorless, odorless, and tasteless gas; density 3.733 g/L at 0°C; liquefies at -153.22°C; solidifies at -157.36°C to a white crystalline substance that has a face-centered cubic structure; critical temperature -63.6°C; critical pressure

54.30 atm; critical density 0.908 g/L; triple point temperature -157.4°C ; triple point pressure 0.722 atm; viscosity at 0°C 0.02327 centipoise; slightly soluble in water; solubility in water, 10.69 mL of the gas in 100mL water at 0°C and 1 atm; velocity of sound 213 m/s at 0°C and 1 atm.

Thermochemical Properties

ΔH_f°	0.0
S°	39.2 cal/degree mol
C_p	4.97 cal/degree mol
ΔH_{vap}	2.17 kcal/mol
ΔH_{fus}	0.327 kcal/mol

Production

Most krypton produced in commercial scale comes from air. Krypton and other inert gases are obtained from air by a distillation-liquefaction process. Different types of air-separation plants varying in design are known for commercial production of nitrogen, oxygen, and inert gases (See Helium).

Krypton also may be recovered from spent fuel rods of nuclear power plants. It is produced, along with xenon, in fission of uranium and plutonium. This process, however, is not a major source of krypton, and the recovered gas also contains radioactive Kr-85 isotope.

Reactions

Krypton is an inert gas element. Its closed-shell, stable octet electron configuration allows zero reactivity with practically any substance. Only a few types of compounds, complexes, and clathrates have been synthesized, mostly with fluorine, the most electronegative element. The most notable is krypton difluoride, KrF_2 [13773-81-4], which also forms complex salts such as $\text{Kr}_2\text{F}_3^+\text{AsF}_6^-$ [52721-23-0] and $\text{KrF}^+\text{PtF}_6^-$ [52707-25-2]. These compounds are unstable at ambient conditions. Krypton also forms clathrates with phenol and hydroquinone. Such interstitial substances are thermodynamically unstable and have irregular stoichiometric compositions (See Argon clathrates).

Analysis

Krypton may be analysed most conveniently by GC/MS. The characteristic masses for its mass spectroscopic identification are 84, 86, and 83, the most abundant natural isotopes of the element. It also may be analyzed by gas-solid chromatography by its retention times.

KRYPTON DIFLUORIDE

[13773-81-4]

Formula: KrF_2 ; MW 121.80; The molecule exhibits linear geometry in gas phase.

Uses

Krypton difluoride is used as a powerful oxidizing agent to oxidize halogen fluorides and gold.

Physical Properties

White tetragonal crystal; sublimes under vacuum at 0°C; decomposes slowly at 25°C; density 3.24 g/cm³; reacts with water; vapor pressure 30 torr at 0°C; slightly soluble in liquid fluorine.

Preparation

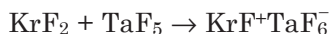
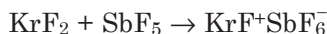
Krypton difluoride may be prepared by the reaction of krypton with fluorine in an electric discharge at low pressure and liquid oxygen temperature. Also it may be made by irradiating krypton with ultraviolet rays in a fluorine—argon gas mixture at liquid helium temperature (−196°F).



The product can be stored at −78°C without decomposition.

Reactions

Krypton difluoride forms complexes with fluorides of many metals, such as arsenic, antimony, tantalum, niobium, gold, and platinum.



Krypton difluoride is a powerful oxidizing and fluorinating agent. For example, it fluorinates ruthenium tetroxide, RuO₄, to ruthenium oxytetrafluoride, RuOF₄, in liquid HF.

Krypton difluoride decomposes into its elements at ambient temperatures.

Analysis

Elemental composition: Kr 68.80%, F 31.20%. Krypton difluoride may be analyzed by GC/MS under cryogenic conditions following its decomposition into its gaseous elements.

LANTHANUM

[7439-91-0]

Symbol: La; atomic number 57; atomic weight 138.91; a rare-earth transition metal, precursor to a series of 14 inner-transition elements known as the lanthanide series; electron configuration [Xe]5d¹6s²; oxidation state +3; atomic radius 1.879Å; ionic radius (La³⁺) 1.061Å; electronegativity 1.17; two natural isotopes are La-139 (99.911%) and La-138 (0.089%).

History, Occurrence, and Uses

Lanthanum was isolated from cerium nitrate in 1839 by Mosander. The element in its oxide form was called “lanthana” meaning “hidden”. Although the electron configuration of the element shows a vacant $4f$ orbital and, therefore, does not belong to the “true rare-earth elements,” the metal exhibits striking similarities to other rare-earths. In nature, lanthanum never occurs in free state and is always found associated with other rare-earth metals. The principal minerals are monazite and bastnasite. Its concentration in the earth’s crust is estimated to be 30 mg/kg. Lanthanum as a pure metal has limited applications. However, in the form of alloys, the metal has several metallurgical applications. When alloyed with iron, chromium, nickel, and molybdenum, it improves resistance of these metals to oxidation. It also improves the impact strength, fluidity, ductility and other mechanical properties of the alloys. The pure metal is used only for research.

Physical Properties

Silvery white metal; soft and malleable; hexagonal closed pack crystal system; transforms to face-centered cubic crystals at 310°C which further transforms to a body-centered cubic allotropic modification at 868°C; density 6.166 g/cm³; Brinell hardness (as cast) 37; melts at 918°C; vaporizes at 3,464°C; vapor pressure 1 torr at 2,192°C; electrical resistivity 56.8 x 10⁶ ohm-cm at 25°C; Young’s modulus 3.84 x 10⁻¹¹ dynes/cm²; Poisson’s ratio 0.288; thermal neutron cross section 8.9 barns.

Thermochemical Properties

ΔH_f° (cry)	0.0
S° (cry)	13.6 cal/degree mol
C_p (cry)	6.48 cal/degree mol
ΔH_f° (g)	103.0 kcal/mol
ΔG_f° (g)	94.1 kcal/mol
S° (g)	43.56 cal/degree mol
C_p (g)	5.44 cal/degree mol
ΔH_{fus}	2.75 kcal/mol
ΔH_{vap}	100.8 kcal/mol
$\Delta H_{transformation}$ (alpha-beta)	0.095 kcal/mol
Thermal conductivity (at 28°C)	0.033 cal/cm ² /cm/sec/°C
Coeff. thermal expansion (at 400°C)	7.9 x 10 ⁻⁶ /°C

Production

Lanthanum is most commonly obtained from the two naturally occurring rare-earth minerals, monazite and bastnasite. Monazite is a rare earth-thorium phosphate that typically contains lanthanum between 15 to 25%. Bastnasite is a rare earth-fluocarbonate-type mineral in which lanthanum content may vary, usually between 8 to 38%. The recovery of the metal from either of its ores involves three major steps: (i) extraction of all rare-earths combined together from the non-rare-earth components of the mineral, (ii) separation or isolation of lanthanum from other lanthanide elements present

in the mineral extract, and (iii) preparation of high-purity grade lanthanum from its isolated product.

Industrial production processes also may vary depending on the nature and availability of mineral, manufacturing cost, demand for other by-products, purity level of the metal desired, and its end use. Recovery processes are quite similar to other rare-earth metals and chemistry of the processes does not differ noticeably from one metal to another.

Extraction of lanthanum from monazite is discussed below first, followed by that from bastnasite.

The mineral mixtures are crushed and ground. Monazite, because of its magnetic properties, may be separated from other minerals that may be either magnetic or nonmagnetic by repeated electromagnetic separation using electromagnets of varying intensities. After its separation the mineral is treated with hot concentrated sulfuric acid, which converts thorium, lanthanum, and rare-earth metals present into their sulfates. These sulfates are soluble in water. The soluble products are leached into water. The insoluble residues and impurities are filtered out. Then the acidic filtrate is partially neutralized with caustic soda to pH 3 to 4. Thorium precipitates out of solution as hydroxide. Alternatively, thorium may be precipitated as pyrophosphate by adding sodium pyrophosphate to the acid solution. The solution after removal of thorium is treated with ammonium oxalate. This converts all lanthanide elements in the ore into their insoluble oxalate salts. The oxalates decompose into oxides when calcined in air. Cerium is the major component of this mixture of rare-earth oxides. Also, it is the only lanthanide element oxidized to its tetravalent state, Ce^{4+} . The tetravalent cerium(IV) oxide is insoluble in dilute nitric acid. The oxide mixture is, therefore, treated with dilute nitric acid to dissolve lanthanum oxide and other rare-earth oxides to separate them from cerium. Lanthanum is separated from this cerium-free rare-earth mixture as a double salt with ammonium nitrate by crystallization. The lanthanum-ammonium double salt is relatively less soluble than other rare-earth double salts and stays in the most insoluble fraction.

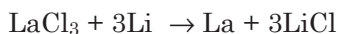
The most efficient method of separating lanthanum from rare-earth salts solution involves ion exchange. In this process, lanthanum and other tripositive rare-earth metal ions are sorbed onto suitable cation-exchange resin beds by exchange with hydrogen, ammonium, or cupric ions incorporated into the resins. The rare-earth ions are then selectively removed in successive steps by eluting with solutions of suitable complexing agents. Several complexing agents have been used successfully. These include ammonium citrate (a buffered solution, pH 2-4); buffered nitrilotriacetate; buffered ethylenediamine tetraacetic acid (EDTA); and ammonium or metal salts of EDTA. Buffered solution of ammonium-EDTA (pH ~8.4) has been found to be highly effective in such ion-exchange separation, yielding high purity products. EDTA complexes of lanthanide elements have high formation constants in a significantly wide range, between 10^{14} and 10^{19} .

Lanthanum also may be separated from aqueous solutions of rare-earth nitrates by liquid-liquid extraction using a suitable water-immiscible organic liquid such as tributyl phosphate or another complexing agent dissolved in it.

The method, however, is not as efficient as the ion-exchange technique discussed above.

Lanthanum in purified metallic state may be obtained from its purified oxide or other salts. One such process involves heating the oxide with ammonium chloride or ammonium fluoride and hydrofluoric acid at 300° to 400°C in a tantalum or tungsten crucible. This is followed by reduction with alkali or alkaline earth metals at 1,000°C under argon or in vacuum.

A typical reaction is:



Also high purity lanthanum may be produced by electrolysis of a molten mixture of anhydrous lanthanum chloride and sodium chloride or potassium chloride at elevated temperatures.

When lanthanum is produced from the mineral bastnasite, all processes except ore extraction discussed above are the same. The mineral is crushed and concentrated by flotation process. This is followed by treatment with dilute HCl, which converts lanthanum and the rare-earths contained in the mineral into their chlorides. Calcination in air results in rare-earth oxides.

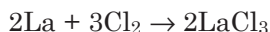
Reactions

Lanthanum metal forms salts in +3 oxidation state, the only stable valence state of this element. The redox potential for the reaction $\text{La} \rightarrow \text{La}^{3+} + 3\text{e}^-$ in aqueous phase is 2.522 V. The La^{3+} ion is colorless.

Combustion in air or oxygen produces lanthanum sesquioxide. However, at ambient temperatures, when exposed to moist air, the metal forms a hydrated oxide with a large volume increase.

Lanthanum reacts with water forming its hydroxide, $\text{La}(\text{OH})_3$. The reaction is slow in cold water but faster in hot water.

Lanthanum reacts vigorously when heated with halogens above 200°C, forming lanthanum halides:



With hydrogen, interstitial hydrides are formed, the compositions of which may vary from LaH_2 to LaH_3 .

Lanthanum combines with nitrogen, carbon, sulfur and phosphorus at elevated temperatures, forming binary salts. Also, with metalloid elements such as boron, silicon, selenium, and arsenic, similar reactions occur at high temperatures forming similar binary compounds.

Analysis

The element may be analyzed by several instrumental techniques including atomic absorption and emission spectrophotometry, ICP-MS, x-ray fluorescence, and neutron activation analysis.

LANTHANUM CHLORIDE

[10099-58-8]

Formula: LaCl_3 ; MW 245.26; forms a stable heptahydrate, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, [20211-76-1], MW 371.37.

Uses

Lanthanum chloride is used to prepare other lanthanum salts. The anhydrous chloride is employed to produce lanthanum metal.

Physical Properties

The anhydrous chloride is a white hexagonal crystal; hygroscopic; density 3.84 g/cm^3 ; melts at 850°C ; soluble in water. The heptahydrate is a white triclinic crystal; decomposes at 91°C ; soluble in water and ethanol.

Thermochemical Properties

ΔH_f°	-255.6 kcal/mol
C_p	26.0 kcal/mol

Preparation

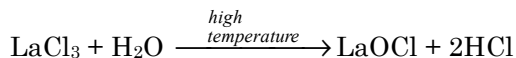
The heptahydrate is formed by dissolving the oxide, hydroxide or carbonate in hydrochloric acid, followed by crystallization. The anhydrous chloride is obtained by heating oxide, hydroxide, or carbonate in an atmosphere of dry hydrogen chloride.



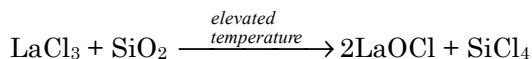
Another method involves heating lanthanum oxide with excess ammonium chloride at 300°C :

Reactions

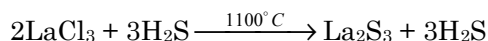
When heated in the presence of water vapor, lanthanum oxochloride is formed:



Heating with glass at elevated temperatures also forms oxochloride:

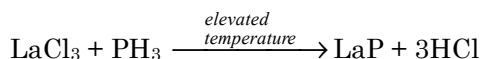


Lanthanum chloride reacts with hydrogen sulfide when heated at 1100°C , forming lanthanum sulfide:

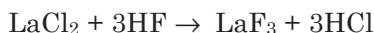


Reactions with ammonia and phosphine at elevated temperatures yield

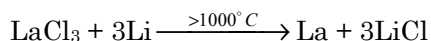
lanthanum nitride and phosphide, respectively:



The addition of hydrofluoric acid to an aqueous solution of lanthanum chloride precipitates out lanthanum fluoride, LaF_3 :



Lanthanum chloride is reduced to lanthanum metal when heated with an alkali or alkaline earth metal at temperatures above 1000°C :



Analysis

Elemental composition: La 56.63%, Cl 43.36%. The salt and its hydrate may be characterized by x-ray methods. Water of crystallization may be determined by gravimetry. Lanthanum may be analyzed by flame or furnace AA or by ICP-AES methods (See Lanthanum). Chloride ion in an aqueous solution of the salt may be measured by titration with a standard solution of silver nitrate or mercuric nitrate or by ion chromatography following appropriate dilution.

LANTHANUM FLUORIDE

[13709-38-1]

Formula: LaF_3 ; MW 195.90

Uses

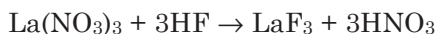
Lanthanum fluoride is used in phosphor lamp coating. Mixed with other rare earths, it is used in carbon arc electrodes and lasers. Also, the fluoride is used in the production of lanthanum metal, an intermediate step in the manufacture of high purity metal.

Physical Properties

White hexagonal crystal; hygroscopic; density 5.9 g/cm^3 ; melts at $1,493^\circ\text{C}$; insoluble in water and acids.

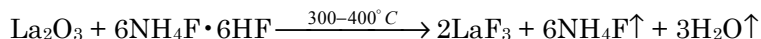
Preparation

Lanthanum fluoride may be precipitated by adding hydrofluoric acid to an aqueous solution of lanthanum nitrate or chloride:



The compound also can be made by heating lanthanum oxide with ammoni-

um fluoride in hydrofluoric acid at 300 to 400°C. Ammonium fluoride released in the reaction sublimes at this temperature:



Anhydrous lanthanum fluoride also may be made by passing dry hydrogen fluoride over lanthanum oxide. This process, however, produces trace amounts of lanthanum oxyfluoride, LaOF. Highly purified material may be obtained by passing dry purified HF over molten fluoride in a platinum crucible.

Analysis

Elemental composition: La 70.91%, F 29.01%. The compound may be characterized by x-ray methods. Lanthanum may be analyzed by AA or ICP technique following digestion in nitric acid and appropriate dilution of acid extract.

LANTHANUM HYDROXIDE

[14507-19-8]

Formula: La(OH)₃; MW 189.93

Uses

Lanthanum hydroxide is used to prepare other lanthanum salts.

Physical Properties

White amorphous solid; decomposes on heating; insoluble in water.

Preparation

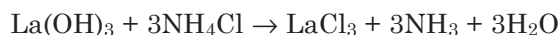
Lanthanum hydroxide is precipitated by adding excess of caustic soda, caustic potash or ammonia to an aqueous solution of a La³⁺ salt, such as LaCl₃, La(NO₃)₃ or La(SO₄)₃:



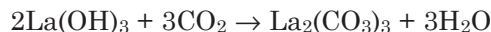
Reactions

The hydroxide is strongly basic. It reacts with acids undergoing neutralization reactions; i.e., reaction with HCl or HNO₃ yields hydrated salt of lanthanum chloride or nitrate on evaporation and crystallization of the solution.

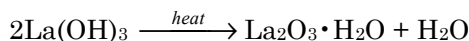
It reacts with ammonium salts displacing ammonia:



The hydroxide absorbs CO₂ from air forming lanthanum carbonate:



Lanthanum hydroxide on dehydration produces lanthanum oxide monohydrate, $\text{La}_2\text{O}_3 \cdot \text{H}_2\text{O}$:



Analysis

Elemental composition: La 73.13%; O 25.27%, H 1.59%. Lanthanum may be analyzed in the acidified extract of the compound by AA or ICP technique (See Lanthanum). Dehydration at 100°C produces $\text{La}_2\text{O}_3 \cdot \text{H}_2\text{O}$, releasing one mole of water of crystallization per mole of hydroxide (9.5%) loss, which may be measured by gravimetry.

LANTHANUM NITRATE

[10277-43-7]

Formula: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; MW 433.01; stable as hexahydrate

Synonym: lanthanum nitrate hexahydrate

Uses

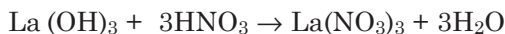
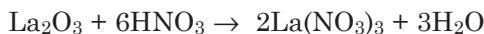
The nitrate is used as an analytical standard; as a matrix modifier in furnace AA analysis; and for preparing other lanthanum salts.

Physical Properties

White crystalline solid; hygroscopic; decomposes around 40°C; very soluble in water and alcohol.

Preparation

The salt is prepared by dissolution of lanthanum oxide, hydroxide or carbonate in nitric acid, followed by crystallization, and obtained as a hexahydrate. The general reactions are as follows:



Reactions

Thermal dissociation yields lanthanum oxide, La_2O_3 . Its reactions in aqueous solutions are those of La^{3+} ion. It forms double salts with magnesium, calcium and ammonium nitrates and many other salts when mixed in stoichiometric amounts. Such double salts are obtained from solution mixtures on crystallization and may vary in their compositions.

Analysis

Elemental composition (for hexahydrate): La 32.08%, N 9.70%, H 2.79%, O

55.43%. The water of crystallization may be determined by heating a weighed quantity of the salt and measuring the loss in weight by gravimetry. Lanthanum may be analyzed in a dilute aqueous solution by AA or ICP spectrophotometry. N, H and O may be determined by elemental analysis.

LANTHANUM OXIDE

[1312-81-8]

Formula: La_2O_3 ; MW 325.81

Synonyms: lanthanum trioxide; lanthanum sesquioxide; lanthana

Uses

Highly pure lanthanum oxide is used to make optical glass of high refractive index for camera lenses. It also is used to make glass fibers. The oxide also is used to improve thermal and electrical properties of barium and strontium titanates. Other applications are in glass polishes; carbon arc electrodes; fluorescent type phosphors; and as a diluent for nuclear fuels. In such applications, lanthanum oxide is usually combined with other rare earth oxides.

Physical Properties

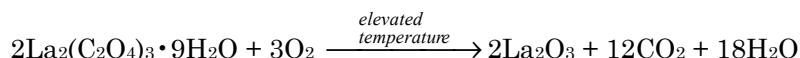
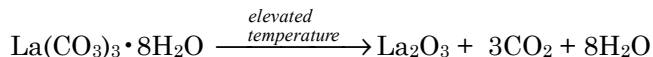
White amorphous powder; density 6.51 g/cm³; melts at 2,305°C; vaporizes at 4,200°C; insoluble in water; dissolves in dilute mineral acids.

Thermochemical Properties

ΔH_f°	-428.7 kcal/mol
ΔG_f°	-407.7 kcal/mol
S°	30.43 cal/degree mol
C_p	26.00 cal/degree mol

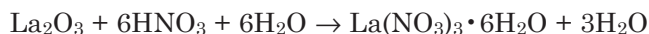
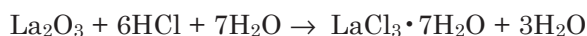
Preparation

Lanthanum oxide can be produced by direct combustion of lanthanum in oxygen or air. The oxide also may be prepared by decomposition of an oxo salt of lanthanum, such as nitrate, sulfate, carbonate, hydroxide or oxalate.



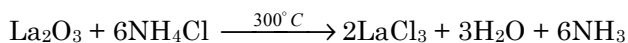
Reactions

The oxide reacts with acids forming their salts:



The hydrated salts contain the ions $[\text{La}(\text{H}_2\text{O})_n]^{3+}$.

Heating the oxide with an excess of ammonium chloride yields lanthanum chloride:



Reaction with strong alkalis at high temperature and pressure slowly forms crystals of lanthanum hydroxide, $\text{La}(\text{OH})_3$.

Analysis

Elemental composition: La 85.27%, O 14.73%. The compound may be characterized by x-ray. Lanthanum may be analyzed by various instrumental techniques (See Lanthanum).

LANTHANUM SULFATE

[10294-62-9]

Formula: $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$; MW 728.14; stable as nonhydrate

Synonym: lanthanum sulfate nonhydrate

Uses

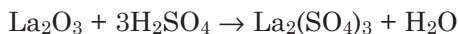
Lanthanum sulfate is used to prepare many lanthanum compounds.

Physical Properties

White hexagonal crystals; density 2.82 g/cm³; slightly soluble in cold water, solubility decreasing with temperature; insoluble in ethanol; dehydrates in the air at 400°C.

Preparation

Lanthanum sulfate is prepared by dissolving lanthanum oxide, hydroxide or carbonate in sulfuric acid, followed by crystallization.



Analysis

Elemental composition (for nonhydrate, $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$): La 38.15%, S 13.21%; H 2.49%, O 46.14%. Water of crystallization 22.27%. The compound is digested in nitric acid, the acid extract diluted and analyzed for lanthanum by AA or ICP (See Lanthanum). The water of crystallization may be determined by measuring loss of water by gravimetry following dehydrating a weighted amount of substance at 400°C. Also, the solid crystals may be characterized by x-ray.

LAWRENCIUM

[22537-19-5]

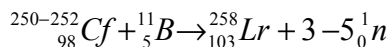
Symbol: Lr; atomic number 103; atomic weight 262; a transuranium inner-transition actinide series element; a synthetic radioactive element; electron configuration $[\text{Rn}]7s^25f^{14}6d^1$; valence +3; six isotopes of masses 255 to 260 have been synthesized; longest-lived known isotope Lr-260 has half-life of ~3 minutes.

History

Lawrencium was synthesized by Ghiorso, Sikkeland, Larsh and Latimer in 1961 in Lawrence Radiation Laboratory, Berkeley, California. The new element was named after Ernest O. Lawrence. The element has no practical application.

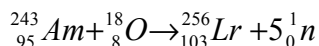
Synthesis

Lawrencium has been synthesized only in very minute quantities. It was first synthesized by irradiating a mixture of californium isotopes with boron ions:



The isotope obtained this way has a half-life of about 4.2 seconds and is an alpha emitter.

Lawrencium-256 (~35 seconds) is prepared by bombarding americium-243 with oxygen-18:



All lawrencium isotopes of masses 255 to 260 have been synthesized by bombardment of transuranium elements with heavy ions.

LEAD

[7439-92-1]

Symbol Pb; atomic number 82; atomic weight 207.20; a Group IV A (Group 14) metallic element; metallic radius 1.75 Å; covalent radius (sp³) 1.44 Å; ionic radius Pb²⁺ 1.18 Å; Pb⁴⁺ 0.70 Å; electron configuration $[\text{Xe}]4f^{14}5d^{10}6s^26p^2$; valence +2 and +4. Four stable isotopes are known: Pb-204 (1.48%), Pb-206 (23.6%), Pb-207 (22.6%) and Pb-208(52.3%); three of these (Pb-206, Pb-207 and Pb-208) are the end products of uranium, actinium and thorium series, respectively. Twenty-seven (27) radioisotopes are known.

History, Occurrence, and Uses

Lead is one of the oldest metals known to civilization. The uses of some of its alloys and salts have been documented early in history. The ele-

ment derived its symbol Pb from the Latin word plumbium. The metal is rarely found in nature in its native form; however, it is found in several minerals, such as galena (PbS), anglesite (PbSO₄), minium (Pb₃O₄) and cerussite (PbCO₃). Its concentration in the earth's crust is 12.5 mg/kg and in sea water 0.03mg/L.

Lead has numerous applications as metal, alloys and compounds. The major applications of the metal and its alloys such as solder are as materials of construction for pipe lines, plumbing fixtures, wires, ammunition, containers for corrosive acids and shield against short-wavelength radiation. Another major application is in storage batteries in which both the metal and its dioxide are used. Several lead compounds, such as lead chromate (chrome yellow), lead sulfate (white lead), lead tetroxide (red lead), and the basic carbonate are used in paints.

Physical Properties

Silvery grey metal with bright luster; face-centered cubic crystals; very soft, malleable and ductile; easily cast, rolled and extruded; density 11.3 g/cm³; Moh's hardness 1, Brinell hardness 4.0 (high purity metal); easily melted, melts at 327.46°C; vaporizes at 1,749°C; vapor pressure 1 torr at 970°C and 10 torr at 1160°C; poor conductor of electricity; electrical resistivity 20.65 microhm-cm at 20°C and of liquid melt 94.6 microhm-cm at its melting point; viscosity of molten metal 3.2 centipoise at its melting point and 2.32 centipoise at 400°C; surface tension 442 dynes/cm at 350°C; tensile strength 2,000 psi; thermal neutron absorption cross section 0.17 barn; standard electrode potential, $\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$ -0.13V; very resistant to corrosion.

Thermochemical Properties

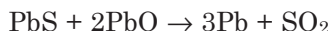
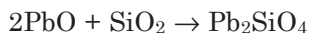
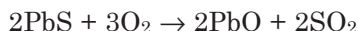
ΔH_f° (cry)	0.0
ΔH_f° (gas)	46.65 kcal/mol
ΔG_f° (gas)	38.77 kcal/mol
S° (cry)	15.49 cal/degree mol
S° (gas)	41.92 cal/degree mol
C_p (cry)	6.31 cal/degree mol
C_p (gas)	4.97 cal/degree mol
ΔH_{fus}	1.14 kcal/mol
ΔH_{vap}	49.9 kcal/mol
Thermal conductivity	
at 18°C	0.083 cal/cm ² /sec/cm/°C
at 330°C	0.039 cal/cm ² /sec/cm/°C
Coefficient of linear expansion	$2.9 \times 10^{-6}/^\circ\text{C}$

Production

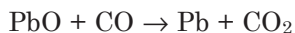
Lead is produced commercially from its principal ore, galena (PbS). The ore is associated with sulfides of several metals including iron, copper, zinc, silver, bismuth, arsenic, antimony and tin. The ore is crushed and ground. It then is selectively separated from gangue and other valuable minerals by one or more processes that include gravity separation and flotation. Selective

flotation processes are most commonly employed to remove significant quantities of most metal sulfides, silica, and other impurities. This yields relatively pure galena concentrate containing 50 to 80% lead.

The lead concentrate must be roasted for effective removal of sulfur and then smelted in a blast furnace. Sulfur is mostly removed by a sinter process. The galena concentrate or the ore itself, if its impurity content is low, is mixed with silica and other slag-forming reagents and roasted in sinter machines to produce lead oxide, lead silicate, and some metallic lead. The principal reactions are:



Lead oxide, silicate, and the gangue material consisting of silica, lime, iron oxide, zinc oxide and alumina, react in a blast furnace at 1,000°C, producing lead (lead bullion) along with matte and speiss that result from reactions of residual sulfur with copper and arsenic. Slag, dust, and gases (CO and CO₂) are the other products generated in the blast furnace. The principal reactions in the furnace are:



Lead bullion obtained from the blast furnace contains copper and other metals which may be removed either by pyrometallurgical methods or by electrolysis. Copper mostly is removed by cooling the bullion from the furnace to 350°C at which temperature it becomes insoluble and separates out. Trace copper left in the lead eutectic mixture is removed by addition of elemental sulfur to form copper sulfide. Arsenic, antimony, and tin may be removed either by Harris process, involving pumping the lead bullion through molten sodium hydrate, or by a “softening” process that involves blowing air over molten bullion at 750°C, whereby these metals are converted into their oxides and form slags. Silver and gold may be removed either by Parkes process or the old Pattinson process. In the Parkes process, molten zinc is added to the molten lead bullion. Zinc forms alloys with silver and gold and rises to the top as a crust that also contains some lead. The crust is distilled in a retort to free zinc metal for reuse. Trace zinc is removed from the lead bullion either as zinc chloride, by treatment with chlorine gas, or by vacuum distillation. The last

remaining bismuth metal is separated by Kroll-Betterton process. In this process, calcium and magnesium are added into the lead bullion. They form calcium and magnesium bismuthides, Ca_3Bi_2 and Mg_3Bi_2 , respectively, which are removed as dross. Refined bismuth may be obtained from this dross.

Electrolytic refining of lead bullion is commonly employed in many modern plants to obtain high purity grade metal. Various separation processes for removal of individual metals are not required. In such refining (Betts process), a solution of lead fluosilicate is used as an electrolyte, while the anode consists of impure lead bullion and the cathode constitutes a thin sheet of pure lead. Lead deposits on to the cathode during electrolysis. Impurity metals remain undissolved and attached to the anode, forming a slime which may be removed after electrolysis and treated for recovery of these metals.

Reactions

Lead forms amphoteric compounds in +2 and +4 valence states, forming plumbous and plumbic salts, such as PbCl_2 and PbCl_4 , as well as plumbites and plumbates, such as Na_4PbO_3 and Ca_2PbO_4 . Over a thousand compounds of lead are known which include divalent and tetravalent salts, complexes, and organometallics. Divalent compounds of lead are far more numerous than the tetravalent compounds. Most compounds, however, result from the reactions involving other lead compounds, rather than elemental lead. Only the reactions involving elemental lead are outlined briefly below.

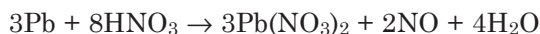
In very finely divided form, lead is pyrophoric. When heated in oxygen or air, the metal forms lead monoxide, PbO , which is oxidized further in the presence of excess oxygen or air to lead tetroxide, Pb_3O_4 . The finely divided metal dissolves in a solution of sodium in liquid ammonia, forming a green solution of Na_4Pb_9 .

The metal is not attacked by hot water. But in the presence of free oxygen, lead(II) hydroxide is formed. The overall reaction is:



In hard water, however, the presence of small amounts of carbonate, sulfate, or silicate ions form a protective film on the metal surface, and prevent the occurrence of the above reaction and thus, corrosion of the metal.

Lead does not evolve hydrogen readily with acids. Nitric acid attacks the metal readily, forming lead nitrate and oxides of nitrogen:



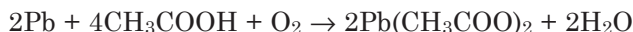
This reaction is faster in dilute nitric acid than strong acid. Hydrochloric acid has little effect on the metal. At ordinary temperatures, lead dissolves slowly in hydrochloric acid, forming a coating of lead(II) chloride, PbCl_2 over the metal, which prevents further attack.

At ordinary temperatures, lead is not readily attacked by sulfuric acid. A coating of insoluble lead sulfate formed on the metal surface prevents any further reaction of the metal with the acid. The acid is, therefore, stored in spe-

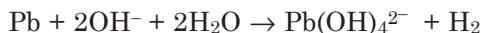
cially designed lead containers. Also, the action of hot concentrated sulfuric acid is very low up to about 200°C. However, at temperatures near 260°C, both the concentrated sulfuric and hydrochloric acids dissolve lead completely.

At ordinary temperatures, hydrofluoric acid also has little action on the metal. Formation of insoluble PbF_2 prevents dissolution of lead in the acid.

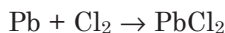
Organic acids in the presence of oxygen react slowly with lead, forming their soluble salts. Thus, acetic acid in the presence of oxygen forms lead(II) acetate:



Lead dissolves in alkalies forming plumbite ion, $\text{Pb}(\text{OH})_4^{2-}$ with the evolution of hydrogen:

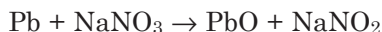


Lead combines with fluorine, chlorine, and bromine, forming bivalent lead halides:



Fusion with sulfur at elevated temperatures yields lead sulfide, PbS .

The metal is oxidized to PbO when heated with sodium nitrate at elevated temperatures.



Lead is widely used in storage batteries. Each cell consists of a spongy lead plate as cathode and lead dioxide as anode immersed in the electrolyte sulfuric acid. The overall chemical reaction in the cell during discharge is as follows:



Analysis

A number of methods have been described in old literature based on colorimetry and gravimetry. Such methods apply to measuring soluble lead(II) salts in water. One method involves precipitating Pb^{2+} using chromic acid to obtain yellow lead chromate. Dithizone colorimetric method is very sensitive in measuring lead in water. The method involves acidifying the sample, mixing with ammoniacal citrate-cyanide reducing solution, and extracting with dithizone in chloroform to a cherry-red derivative and measuring absorbance at 510 nm using a spectrophotometer. The most sensitive and accurate measurements, however, involve instrumental techniques. Lead may be analyzed in aqueous matrices or the nitric acid extracts of its salts by flame and furnace

AA, ICP-AES, and ICP/MS techniques. The measurements are done at the wavelengths 283.3 and 217.0 nm for flame and furnace AA and 220.35 and 217.00 nm for ICP-AES analyses. The instrument detection levels are high ppb range for flame AA and low ppb by furnace AA and ICP-AES, and much lower for ICP-MS.

Lead may be analyzed both in aqueous and nonaqueous matrices by x-ray techniques. High concentration of the metal in paint chips can be measured rapidly and nondestructively by x-ray fluorescence.

Lead in water may be analyzed very precisely at low concentrations by anodic stripping voltametry using an electrochemical analyzer; static or controlled growth mercury drop electrodes, reference calomel or silver-silver chloride electrodes; and silica or TFE cells. Copper, silver, gold, and certain organic compounds may interfere in the test. (APHA, AWWA and WEF. 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, D.C.: American Public Health Association.)

Lead also may be measured by neutron activation analysis.

Toxicity

Lead is an acute and a chronic toxicant. Acute effects are ataxia, headache, vomiting, stupor, hallucination, tremors and convulsions. Chronic symptoms from occupational exposure include weight loss, anemia, kidney damage and memory loss. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons.) Permanent brain damage has been noted among children. Lead bioaccumulates in bones and teeth. The metal is classified as an environmental priority pollutant by the US EPA.

The action level for lead in drinking water is 15µg/L. Its content in food and house paints is regulated in the USA by the Food and Drug Administration.

LEAD ACETATE

[301-04-2]

Formula: $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$; MW 325.29; also forms trihydrate $\text{Pb}[\text{C}_2\text{H}_3\text{O}_2]_2 \cdot 3\text{H}_2\text{O}$ and decahydrate $\text{Pb}[\text{C}_2\text{H}_3\text{O}_2] \cdot 10\text{H}_2\text{O}$

Synonyms: lead(II) acetate; plumbous acetate; normal lead acetate; neutral lead acetate; sugar of lead

Uses

Being the most soluble salt of lead, lead acetate is used extensively as starting material to prepare several other lead salts. It is used to produce basic lead acetates and basic lead carbonate for making pigments. The compound itself is used as a mordant for dyeing and printing cottons; in lead coating of metals; in the manufacture of lead driers for paints; as a sedative and astringent in medicine; in cosmetics, perfumes and toiletries; and in analytical chemistry for detection of sulfide.

Physical Properties

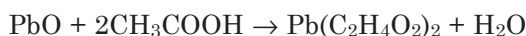
The anhydrous salt is a white crystalline solid; very sweet taste; density 3.25 g/cm³ at 20°C; melts at 280°C; very soluble in cold water (44.39g/100g at 20°C); solubility is much greater in hot water (221g/100g at 50°C; also soluble in alcohols.

The trihydrate is a colorless monoclinic crystal or white granule or powder; refractive index 1.567 (along the beta axis); faint vinegar odor; intense sweet taste and then metallic after-taste; slowly effloresces; density 2.55 g/cm³; melts at 75°C upon rapid heating; loses some of its water of crystallization on heating which dissolves in it; decomposes at 200°C; highly soluble in water (45.61g/100g at 15°C and 200g/100g at 100°C); insoluble in alcohol.

The decahydrate is white rhombic crystal; density 1.69 g/cm³; melts at 22°C; soluble in water but insoluble in alcohol.

Preparation

Lead acetate is prepared by dissolving lead monoxide in strong acetic acid:



The trihydrate is obtained by dissolving lead monoxide in hot dilute acetic acid solution. Upon cooling, large crystals separate out.

Reactions

Exposure to carbon dioxide yields basic lead carbonate, 2PbCO₃•Pb(OH)₂, the composition of which may vary with reaction conditions.

Reactions with sulfuric acid, hydrochloric acid and hydriodic acid yield lead sulfate PbSO₄, lead chloride PbCl₂, and lead iodide PbI₂, respectively.

Reaction with hydrogen sulfide forms black precipitate of lead sulfide, PbS. A paper soaked with lead acetate solution turns black on exposure to H₂S, a test often used to detect sulfide.

Analysis

Elemental composition: Pb 63.70%, C 14.77%, H 1.86%, O 19.97%. The compound may be identified from its physical properties and elemental analysis of C, H, O and Pb. Lead is analyzed by AA, ICP, x-ray fluorescence and other instrumental methods (See Lead).

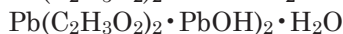
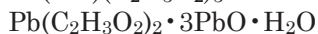
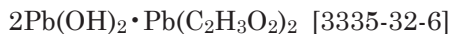
Toxicity

Moderately toxic by intraperitoneal route and possibly by oral route.

LD₅₀ intraperitoneal (mouse): 400 mg/kg

LEAD ACETATES, BASIC

Several basic lead acetates are known with varying compositions of acetate, hydroxide ions, and/or water of crystallization. Some of them are:



These basic acetates are used in the manufacture of pigments; in dyeing and printing fabrics, the aqueous solutions in medicine for washes and poultices; in sugar analysis; and as starting materials for preparing other lead salts.

The basic acetates are heavy white powders; decompose on heating; readily dissolve in water; and have low to moderately high solubility in ethanol.

Preparation

Basic lead acetates are prepared by dissolving lead monoxide in hot dilute acetic acid, or by dissolving the oxide in dilute acetic acid at alkaline pH. They may be made by dissolving lead monoxide in a solution of lead acetate. Crystalline products are obtained upon cooling the solutions.

Analysis

The composition of the salts is determined by elemental analysis including that of lead and x-ray methods. The water of crystallization may be measured by gravimetry.

LEAD AZIDE

[13424-46-9]

Formula: $\text{Pb}(\text{N}_3)_2$; MW 291.24

Uses

Lead azide is used in fuses and detonators as a primary explosive to initiate the booster. It also is used in shells and cartridges.

Physical Properties

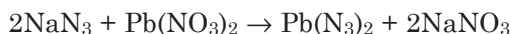
Colorless needles or white powder; density $\sim 4.0 \text{ g/cm}^3$; explodes on heating at 350°C ; slightly soluble in water, 230 mg/L at 18°C and 900 mg/L at 70°C ; very soluble in acetic acid; insoluble in ammonia solution.

Thermochemical Properties

$$\Delta H_f^\circ \quad 110.5 \text{ kcal/mol}$$

Preparation

Lead azide is prepared by the reaction of sodium azide with lead nitrate:



Analysis

Elemental composition: Pb 71.14%, N 28.86%. Lead azide is digested cau-

tiously in nitric acid under mild heating. The solution is diluted and analyzed for lead by various instrumental techniques (See Lead).

Hazard

Lead azide explodes on heating at 350°C or on percussion. Its detonation velocity is 5.1 km/sec (Meyer, E. 1989. *Chemistry of Hazardous Materials*, 2nd ed. Englewood Cliffs, N.J.: Prentice Hall). It undergoes violent explosive reaction with carbon disulfide and forms shock-sensitive copper and zinc azides when mixed with the solutions of copper and zinc salts (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley).

LEAD BROMIDE

[10031-22-8]

Formula: PbBr₂; MW 367.01

Synonym: lead dibromide; lead(II) bromide

Uses

Lead bromide is used for developing images in photography; as inorganic filler in fire-retardant plastics; as a photopolymerization catalyst for acrylamide monomer; and as a welding flux for welding aluminum or its alloys to other metals.

Physical Properties

White orthorhombic crystals; density 6.66 g/cm³; melts at 373°C; forms a horn-like mass on solidification; vaporizes at 916°C; decomposes slowly on exposure to light; sparingly soluble in cold water (4.55 g/L at 0°C and 8.44 g/L at 20°C, respectively); moderately soluble in boiling water (44.1g/L at 100°C); K_{sp} 6.60x10⁻⁶ at 25°C; insoluble in alcohol; slightly soluble in ammonia; soluble in alkalies and also in sodium or potassium bromide solutions.

Thermochemical Properties

ΔH_f°	-66.60 kcal/mol
ΔG_f°	-62.60 kcal/mol
S°	38.60 cal/degree mol
C_p	19.15 cal/degree mol

Preparation

Lead bromide is prepared by treating an aqueous solution of lead nitrate with hydrobromic acid or with sodium or potassium bromide:



The solution is allowed to stand to let the precipitate settle.

The compound also may be obtained by adding lead carbonate or lead

monoxide to hydrobromic acid.

Analysis

Elemental composition: Pb 56.45%, Br 43.55%. An aqueous solution may be analyzed for lead by AA or ICP spectroscopy and the bromide ion by ion chromatography, following appropriate dilution.

Toxicity

Moderately toxic by ingestion. The toxic effects are those of lead.

LEAD CARBONATE

[598-63-0]

Formula: PbCO_3 ; MW 267.21

Occurrence and Uses

Lead carbonate occurs in nature as the mineral cerussite. It has several applications. The compound is used in high pressure lubricating greases; as a coating on polyvinyl chloride to improve the dielectric properties of the polymers; in the PVC friction liners for pulleys; in corrosion-resistant grids in lead-storage batteries; in heat-sensitive sheets for thermographic copying; as a photoconductor in electrophotography; in thermistors; and in waxes for steel cables. Another major application of this compound is in catalysis—to catalyze polymerization of formaldehyde to high molecular weight polymeric products and to accelerate the process of curing of moldable thermosetting silicone resins.

Physical Properties

Colorless orthorhombic crystals; refractive index 1.804; Moh's hardness 3–3.5; density 6.60 g/cm³; decomposes on heating at 315°C; practically insoluble in water (1.1 mg/L at 20°C); K_{SP} 1.46×10^{-13} at 25°C; also insoluble in alcohol and ammonia; soluble in acids and alkalies.

Thermochemical Properties

ΔH_f°	−167.1 kcal/mol
ΔG_f°	−149.5 kcal/mol
S°	31.3 cal/degree mol
C_p	20.9 cal/degree mol

Preparation

Lead carbonate is prepared by passing carbon dioxide into a cold dilute solution of lead acetate:

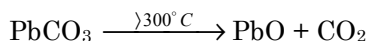


The compound also is prepared in the laboratory by adding sodium bicarbonate to a cold dilute solution of a lead(II) salt, such as lead nitrate or acetate:



Reactions

When heated at 315°C, lead carbonate decomposes to lead oxide and carbon dioxide:



When heated in water, it transforms to basic lead carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$



Lead carbonate dissolves in acids, forming the corresponding lead salt and evolving carbon dioxide:



Reaction with concentrated acetic acid yields anhydrous lead(II) acetate.

Fusion with boric acid at high temperature forms lead metaborate that has an approximate composition $\text{Pb}(\text{BO}_2)_2 \cdot \text{H}_2\text{O}$. The product loses water of crystallization at 160°C.

Analysis

Elemental composition: Pb 77.54%, C 4.49%, O 17.96%. The compound is digested with nitric acid, diluted and analyzed for lead by various instrumental techniques (See Lead). Carbonate may be tested by treating the compound with dilute HCl. It will effervesce, the evolved CO_2 gas will turn limewater milky. Also, liberated CO_2 can be identified using a GC-equipped with a TCD or by GC/MS. The characteristic mass ion for GC/MS identification of CO_2 is 44.

Toxicity

Although an insoluble salt of lead, the compound exhibits low-to-moderate systemic effects from ingestion in humans. The effects are gastrointestinal contractions, jaundice, convulsions, nausea or vomiting, and degenerative changes in the brain (Lewis (Sr.), R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold).